

CERTIFICATE OF TRANSMISSION BY FACSIMILE (37 CFR 1.8)

Applicant(s): Marietta B, Helmeke et al.

Docket No.

DD-043-US-01

Serial No.

09/965,769

Filing Date:

September 27, 2001

Examiner:

Patricia A. Short

Group Art Unit:

1712

Invention:

HOT MELT MOISTURE CURE POLYURETHANE ADHESIVE

WITH WIDE RANGE OF OPEN TIME

I hereby certify that the following is being facsimile transmitted to the United States Patent and Trademark Office to Fax. No. 703-872-9311:

1. Amendment Transmittal Letter, 1 page;

2. Amendment Under 37 CFR 1.116, 5 pages; and

3. Reference, (1), 10 pages.

FAX RECEIVED

JUL 0 1 2003

TC 1700

Julie Post

Typed or Printed Name of Person Signing Certificate

(17) Pages

United States Patent Office

3,043,807 Patented July 10, 1962

3,043,807 POLYUREHANE ELASTOMERS PULYURETHANE ELASTOMIEMS
Carl E. Snyder, Cuyahoga Falls, Nelson V. Scoger, Pulnesville, Ernest E. Fansar, Cuyahoga Falla, and Anthony
F. Finelli and John A. Lovell, Akron, Ohlo, assignors
to The Goodycar Tire & Rubber Company, Akron,
Ohlo, a corporation of Ohlo
No Drawing. Filed Jan. 27, 1958, Ser. No. 711,147
11 Claims. (Cl. 268—75)

This invention relates to improved polyurethane clastomers and to methods for their preparation. More particularly, it relates to polyprethane elastomers which are capable of being cured by means of sulfur and which are capable of being cured by means of sulfur and which 16 are prepared from active-hydrogen-containing linear polymers, organic discovanates and, optionally, a third bifunctional reactant.

The development of rubber products, both solid and cellular, from polyurethanes prepared from the reaction 20 of active-hydrogen-containing linear polymers such as polyesters or polyesteramides and disocyanates has been extensively pursued in recent years. By the term "activehydrogen used to describe the linear polymers employed in the practice of this invention is meant those hydrogen atoms which are reactive as measured and determined by the Zerewitinoff method which includes the hydrogen atoms present in such radicals as the hydroxyl, carboxyl, and thiol radiculs. The physical properties of the up-thane rubbers, particularly in regard to tensile strength and abrasion resistance, have stimulated interest in the use of these rubbers for many industrial applications. In the fabrication of some products from polyurethance it is possible and even advantageous to process the reactants in the form of liquids. For instance, polyurathone foam. products are prepared in this manner, as well as solid molded articles which can be molded directly from the liquid reaction mixture. When, however, the liquid reaction mixture which produces the polyurcthane rubber 40 has to be converted into a solid "ungured" rubber for processing on conventional rubber fabrication equipment such as mix mills or calenders, the chemical nature of the reactants employed to prepare the rubber creates certain problems.

A polyicocyanate, and usually a diffocyanate, is em-ployed to chain-extend the active-hydrogen-containing linear polymer as well as to react with the active-hydrogen atoms along the chain-extended molecule forming cross-links between chains, which cross-linking resction is generally referred to as curing or vulcanization. One approach to the problem of producing a processible polyurethane rubber which can be subsequently cuxed by means of a polyisocyanate is described in United States Patents 2,625,531; 2,625,532; 2,625,535; 2,760,953 and 2,777,831. As described therein, controlled amounts of specific disocyanates are reacted with polyesters and polyesteramides to produce solld rubbers which can be compounded and processed in the same manner as novulcanized natural rubber. One advantage of this type of polyurethane rubber is that it can be stored in the unvulcanized state for extended periods of time until it is to be compounded and processed into a finished prod-During compounding, additional polyisocyanate, which functions as a curing agent, is mixed with the imvulcanized rubber. Following the addition of this second increment of curative polylsocyanate, the rubber must be processed into an article ready for curing within a relatively short time because the reactivity of the iso-cyanate and the exposure of the fully compounded rubher to the accelerative effect of atmospheric moisture

2

contribute to the rather rapid "setting up" of the fully compounded rubber.

It is the broad object of this invention to provide solid unvulcanized polyurethane rubbers which, even after the valcanizing agents have been added thereto, can be stored for extended periods of time without prematurely vulcanizing. Another object is to provide such compounded solid polyurethane rubbers which can be fabricated into uncured products capable of being stored, if desired, for extended periods of time after fabrication and before vulcanization. An additional object is to provide solid unvulcanized polyurethane elastomers which, after curing agents have been added thereto, are not as sensitive to heat and aimospheric moisture as are the known isocyanate-curable polymethane rubbers. Another object is to provide polyurethane clastomers which can be vulcanized to possess outstanding physical properties and which employ chemical vulcanization systems less expensive than the isocyanate system conventionally em-ployed to vulcanize such elastomers. Still another object is to provide volcanization systems for polyurethane elastomers which are chemically more compatible with these conventionally employed with natural rubber and the synthetic elastomeric co-polymers of butadiene and styrene. Another object is to provide liquid or liquid-able unvulcanized vulcanizable polyurathane reaction mixtures which are either liquids at room temperature or capable of being melted at relatively low temperatures, which can be stored for extended periods of time without prematurely vulcanizing and which, without adding other ingredients can be heated, if necessary, to make films, coatings or molded products directly from the liquid state. Other objects will appear as the description procecula.

These and other objects of the invention are accomplished by building into the polyurchane product a pendant or extra-linear group which contains an aliphatic non-benzenoid

group, and preferably a

--d=CH₃

group, capable of reacting with and being cross-linked or vulcanized by reaction with such curing agents as suf-fur or peroxides. Various means are employed to build the pendant-unsaturation-containing component into the polynrethane product.

For instance, pendant unsaturation can be built into a linear polyester before that polyester is modified by the discovenate. By way of exemple, a dibasic acid or a glycol, or both, or a linear ester of either containing extra-linear pendant unsaturation can be esterified to produce a linear polyester containing pendant unsaturation in either or both of the acid or glycol moieties of the

resulting linear polyester.

Alternatively, an settive-hydrogen-containing linear polyester containing no pendent unsaturation can be modified by the diisocyanate in the presence of a third component which contains extra-linear pendant unsaturation and which contains two groups capable of reaction with either the dissocyanate or the terminal groups of the linear polyester or both, examples of such third components being glycols, dicarboxylic acids, or polyesters which contain pendant unsaturation. In addition, an active-hydrogen-containing linear polyester which itself contains no pendant unsaturation can be initially reacted with a diisocyanate to form an isocyanate-terminated linear polyester which is then reacted with a third bi-functional reactant such as a glycol, a dicarboxylic acid or a polyester which contains the pendant unsaturation to yield an ex-

2009/017

tended linear polyurethane molecule with groups conthining pendant rusaturation spaced along the polymer Also, the unvulcanized polyurethane elastomers of this invention can be prepared by employing a discoverante which contains the extra-linear unsaturation. Combinations of two or more of these approaches to "building in" the extra-linear unsaturation represent other modifications employed to prepare the elastomers of this invention.

It has been found that clastomers having outstanding physical properties and which require the use of the least amount of the relatively expensive discovarate are advantageously, prepared from active hydrogen-containing linear polyesters into which pendent unsaturation has been incorporated. This method is preferred since none of the comparatively expensive disocyanale reactant is ecoured to act as the bridging component for the third component which would otherwise have to be employed to incorporate the desired pendant unsaturation into the modified polymer.

When the pendant unsaturation is built into the poly-ester itself, the elastomeric reaction product of this invention may be described essentially as containing recurring structural units of the formula

O is a bivalent radical resulting from the elimination of terminal hydrogen atoms of a glycol;

is a radical resulting from the elimination of terminal hydroxyl groups of a dibasic carboxylic acid;

group for each 6000 units of molecular weight of said elastomeric reaction product, it having been found that if this indicated minimum of

groups is not present in the polymer molecule, the resulting material does not respond to sulfur cure sufficiently to produce the outstanding properties desired in the cured. material.

When the pendant or extra-linear unsaturation is built . into the polymer through the use of a third bifunctional component, the isocyanate groups of the dilsocyanate or the terminal hydroxyl or carboxyl groups of the poly-ester or both react with the functional groups in the third component locating it in and along the polymer chain, if the discoverage, polyester and third compouent are reacted together simultaneously, a so-called random polymer racults with the pendant unsaturation being randomly located along the polymer chain. As indicated above, it is possible and often desirable to tailor the polymer by first reacting the polyester with the disocyanate to form an isocyanate-terminated polyester and then adding the third component carrying the pendant unsaturation with the modified polymer. In this manner it is possible to space the unsaturated groups more evenly along the polymer chain.

An alternative method of building the desired pendant unsaturation into the clastomeric polymers of this invection is to react on acid anhydride containing the unsaturation with a hydroxyl-terminated polyester and to react the acid-terminated polyester thus formed with ethylene oxide to produce a hydroxyl-terminated polyester containing the desired imagination. This, in turn, is reacted with an approximately equal molecular amount of disocyanate to yield the unvulcanized elastomer. This method can be illustrated by the following equations

Uncured signamer

In providing sufficient crosslink points for reaction 80 with sulfur to develop the desired physical properties in the cured material, it has been found that at least one group containing pendant unsaturation must be present in the uncured material for each 6000 units of molecular weight of the reaction product. It is preferred that at 65 least one such pendant group be present for each 1000 to 2000 molecular weight units of the reaction product. It should be apparent that the degree of unsaturation present can be varied by adjusting the amount of bifunc-tional reactant containing the unsaturation employed either to prepare the polyester itself or as a third component in the reaction between the polyester and the dilsocyanate. For instance, a polyester prepared from adigio acid and a mixture of glycols containing 90 molar percent of ethylone glycol and 10 mol percent glycerol-alpha-allyl ether 75 will, if reacted to a molecular weight of approximately.

is a bivalent radical resulting from the addition of two urethane hydrogen atoms to a disocyanate; n is a whole number of such magnitude that the molecular weight of the nolyester segment is from 900 to 5000; X is a radical containing an aliphatic non-banzenoid.

group; m is a whole number including zero and not more than Xm group is attached to a given carbon atom in the radical to which they are attached; the number of X radicals in the molecular structure being such that there is at least one such non-benzenoid alighatic

2000, provide an elastomeric product (after reaction with the discovanate) which will contain approximately one pendant group per each 2000 molecular weight of the product. A similar polyester prepared from a mixture of glycols in which the glycerol-alpha-allyl ether is increased to 20 mol percent will provide approximately one pendant group for each 1000 molecular weight units of the reac-tion product. It should be evident that the actual num-ber of pendant groups can be computed from the molecular weight of the reactants and the molecular weight of the polyester. If the bifunctional reactant containing the pendant unsaturation is corployed as a third component in the reaction with the disocyanate, the number of pendant groups in the product resulting can be readily computed from the molecular weight of the polyester, the molecular weight of the specific bifunctional reactant, the molecularweight of the disocyanate and the weight ratios of these

reactants employed to produce the clastomer.

A wide variety of bifunctional reactants containing extra-linear pendant unsaturation may be employed either in the preparation of the polyester itself or as a third component in the reaction to build in the desired unsaturation. These bifunctional reactants must, in addition to possessing extra-linear unsaturation, contain two groups reactive with the isocyanate radical. Examples of such reactive 25 groups are the hydroxyl group, the carboxyl group, the thiol group and the primary and secondary amino groups. These compounds may be defined by the formula

in which R is an organic radical inert with respect to isocyanate groups, X and Y are selected from the group consisting of -NH2;

-OH; -COOH; and -SH and Z is an organic radical containing the aliphatic non-banzenoid

group. Specific examples of Z are -CH -: CH₂; $-CH_2CH=CH_2;$ $-CH_3-CH=CH-CH_3;$ $-CH_2-CH_3-CH=CH_3;$ $-(CH_2)_n-CH=CH_3$ in which n is a whole number from 1 to 10;

Representative examples of specific bifunctional reactants containing extra-linear pendant unsaturation are:

(1) The hydroxyl compounds such as cryinrol, glycerol-mono-silyl other, glycerol-alpha-allyl ether, allyl ethylene glycol, allyl propylene glycol, bis hydroxyethyl allyloxy succinate, pentacrythritol diallyl ether, vinyl cyclohexane diol, N,N-di(hydroxyethyl) allyl carbamate, dihydroxyethyl allyl carbamate, dihydroxyethyl ethyl ether of 2-allyl hydroquinone; 2,2'-dialiyl P,P' bis-

(2) The dicarboxylic acids such as allyl succinic acid, allyloxysuccinic acid, methollyl succinic acid, and n-octenyl succinic acid.

The preferred bilunctional reactants containing extralinear pendant unsaturation are those which contain the unsaturation as a terminal —CH=CH₂ group which is more reactive with sulfur and which permits a more effec-

tive cross-linking or cure of the polymer.

In addition to the pendant-mashration-containing reactants described above, other glycols and disarboxylic acids or mixtures thereof may be employed to prepare the polyesters used in the practice of this invention. Representative glycols are ethylene glycol; diethylene glycol; 75 desired pendant unsaturation, the actual method of pre-

propylene glycol-1,2; propylene glycol-1,3; butylene glycol-1,4; pentane diol-1,5; decamethylene glycol and N.N-diethanolanillne. Representative seids are those containing at least three carbon atoms such as malonic, succinic, glutaric, adipic, pintelic, suberic, azolaic, sebacic, iso-phthalic, tetrahydrophthalic, hexabydrophthalic, tere-

phthalic and hexaby droterephthalic.

Preferred polyesters are those prepared from adiple acid and ethylene glycol: propylene glycol-1,2; butylene glycol-1,4; or mixtures of these glycols.

The polyesters are prepared by the conventional condemation reaction between the glycol and the acid with

the elimination of water. In order to provide polyesters which are predominantly hydroxyl-terminated and which in no event have acid numbers greater than 5, an excess of glycol (from 10 to 40%) is employed. The polyesters should have an average molecular weight of from 900 to 5000 and preferably from 1500 to 2500.

Any of a wide variety of organic disocyanates may be 20 employed to prepare the polymers of this invention including aromatic, aliphatic and cycloallphatic diisocyanates and mixtures of two or more of these. Representative and intatures in two to more by the compounds include the meta tolylene diisocyanates such as 2,4-tolylene diisocyanate; and 2,6-tolylene diisocyanate; in-phenylene diisocyanate; 4,4'-diphenylene diisocyanate; 4,4'-diphenylene diisocyanate; 1,5-uaphthylene diisocyanate; dianisidine diisocyanate; 4,4'-tolidine cyanate, 4,4'-diphenyl ether disocyanate; 1,4-tetramethylone disocyanate; 1,6-hexamethylene disocyanate; 1,10decamethylene diisocyanate; 1,4-cycloherylene diisocyanate; 4,4'-methylene-bis-(cycloheryl isocyanate) and 1,5tetrahydronaphthylene disocyanate. Of these the arnmatic isocyanates, and particularly the talylene disocyanates, 4,4'-talidine disocyanate and 4,4'-diphenylene methane disocyanate are preferred. The disocyanates may contain other substituents such as alkyl or halogen but should contain no groups such as hydroxyl or amino groups which are reactive with the isocynnate radicals.

In preparing the elastomers of this invention from the 40 polycater, the discovanate and, optionally, the third component containing the pendant unsaturation, it is necesprincit containing the penasini misitalization, it is neces-sary to provide the discovanate in a molecular amount approximately equivalent to the molecular sum of the polyester and the third component, if present. A ratio of from 0.95 to 1.05 mols of discovanate to 1 mol of the other components has been found to produce the de-sired processing characteristics in the resulting unvul-canized polymer. For best processing properties, it is preferred that a very small molecular deficiency of diisocyanate be employed. In particular, if only the disocyanate and polyester are reacted, the preferred amount of discovanate is 0.99 mol per mol of polyester. If a three-component system is employed, the amount of discovenate preferably is equal to the sum of 0.99 mol per mol of polyoster plus the molecular amount of the third component employed. It has been found that, if substantially less than 0.95 or substantially more than 1.05 mols of discovanate per mol of polyester is em-ployed the unvulcanized rubber is either too soft or too 60 mugh to provide completely satisfactory processing on conventional rubber-fabricative equipment such as mills or calcuders, with the softer rubbers being obtained with the smaller amounts of discoverance. Also any discoverance in excess of the recommended substantially equal molecular amounts is available to function as cross-linker for the polymer, cutting down on the desired storage life of both the liquid and solid polymer products.

Depending upon whether the rubber is prepared from

a two-component system (i.e. the disocyanate and a poly-70 ester into which the desired pendant unsaturation has been built) or is prepared from a three-component system in which all or a part of the desired pendant unsaturation is built into the unvulcanized polymer through the use of a third bifunctional reactant containing the

Received from < 651 236 5126 > at 6/30/03 3:57:14 PM [Eastern Daylight Time]

3,043,807

Ð

ture was heated gradually to approximately 100° C, over a period of 20 minutes after which 8.5 parts of phenylbets-naphthylamine was added. The mixture was then baked in an oven for 1½ hours at 110° C. Plasticity tests run on the resulting rubber showed an Olsen flow 6 of 352. The rubber (100 parts) was mixed on a rubber mill with 4 parts mercaptobenzothiazyl disulfide. 1 part mercaptobenzothiazole, 2 parts sulfur and 20 parts high abrasion furnace black. Sheets of the compounded rubber were cured for 90 minutes at 290° F. Tests run on 10 the ctued rubber showed the following properties:

Tensile strength 4400 pounds per square inch.

Elongation at break 570 percent.

Modulus at 300% elongation 2200 pounds per square 15

Shore A durometer hardness... 63.

Example 2

Shore A durometer hardness__ 52.

Example 3

A polyester was prepared from the condensation reaction of one mel of adipic acid, 0.96 mol of ethylene glycol and 0.24 mol of propylene glycol-1,2. This polyester prepared with an approximately 20% excess of glycol had an acid number of 0.5, an hydroxyl number of 59.5 and an average molecular weight of 1870. The polyester (1000 paris) was mixed with 234 parts of 4,4'-tolidine dissocyanate of 99.5% purity. The mixture was heated gradually to approximately 100° C. over a period of 90 minutes after which it was permitted to cool. The resulting isocyanate-terminated prepolymer (538.5 parts) was mixed with 20 parts of crythrol and heated for 14 minutes at 100° C. The mixture was then baked in an oven for 3½ hours at 120° C. Plasticity tests run on the resulting rubber showed an Olsen flow of 176. The rubber (100 parts) was mixed on a rubber null with 4 parts mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazyl disulfide, 1 for mixture was tun on the cured rubber showed the following properties:

Tensile strenih 5800 pounds per square 70 inch.

Elongation at break 800 percent.

Modulus at 300% elongation 500 pounds per equare inch.

Shore A durometer hardness 57. 75

10 Example 4

A polycstar was prepared from the condensation reaction of one mol of adipic acid, 0.96 mol of ethylene glycol and 0.24 mol of propylene glycol-1,2. This polyseter prepared with an approximately 20% excess of glycol had an acid number of 0.5, an hydroxyl number of 59.5 and an average molecular weight of 1870. The polyester (1500 parts) was mixed with 401.5 parts of 4,4°-diphenyl methane diisocyanate of 100% purity. The mixture was heated gradually to approximately 100° C. over a period of 75 minutes after which it was permitted to cool. The resulting isocyanate-terminated prepolymer (439.4 parts) was mixed with 25 parts of glycerol-alpha-allyl eiller and heated for 14 minutes at 100° C. The mixture was then baked in an oven for 16 hours at 120° C. Plasticity tests run on the resulting rubber showed an Olsen flow of 126. The rubber (100 parts) was mixed on a rubber mill with 4 parts mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazole and 2 parts sulfur. Sheets of the compounded rubber were circed for 120 minutes at 300° F. Tests run on the cured rubber showed the following properties:

Tensile strenth 4850 pounds per square inch.
Elongation at break 500 percent: 705 pounds per square inch.

Example 5

A polyester was prepared from the condensation reaction of 1 mol of adipic acid, 0.96 mol of ethylene glycol and 0.24 mol of propylene glycol-1,2. This polyester prepared with an approximately 20% excess of glycol had an acid number of 0.5 and an hydroxyl number of 59.5 and an average molecular weight of 1870. This polyester (1800 parts) was mixed with 511.3 parts of 4,4'-tolidine discoverante having a purity of 99.5%. The mixture was heated gradually to approximately 100° C, over a period of 85 minutes after which it was permitted to cool. The resulting isocyanate-terminated prepolymer (99.5 parts) was mixed with 21.5 parts of bis hydroxychyl allyloxy succinute and heated for 18 minutes at 100° C. The mixture was then baked in an oven at 120° C. for 5½ hours. Plasticity tests run on the rubber resulting showed an Olsen flow of 154. The rubber (100 parts) was mixed on a rubber mill with 4 parts mercaptobonicothizyl disulfide, 1 part mercaptobeniothizole and 2 parts sulfur. Sheets of the compounded rubber were cured for 60 minutes at 300° F. Tests run on the cured rubber showed the following properties:

Tensile strenth 3950 pounds per square nuch.
Elongation at break 715 percent.

55 Modulus at 300% elongation 225 pounds per square nets.

Shore A durometer hardness 54.

Example 6

A polyester was prepared from the condensation reaction of one mal of adipic acid, 0.96 mol of ethylene glycol and 0.24 mol of propylene glycol-1.2. This polyester prepared with an approximately 20% excess of glycol had an acid number of 0.5, an hydroxyl number of 65 59.5 and an average molecular weight of 1870. The polyester (1000 parts) was mixed with 186.3 parts of 2,4-tolylene dilsocyanate of 100% purity. The mixture was heated gradually to approximately 100° C. over a period of 85 minutes after which it was permitted 70 to cool. The resulting isocyanate-terminated prepolymer (312.5 parts) was mixed with 20 parts of glycerol-alpha-allyl other and heated for 26 minutes at 100° C. The mixture was then baked in an oven for 25 hours at 120° C. Plasticity tests run on the resulting rubber showed 75 an Olson flow of 91. The rubber (100 parts) was mixed

8.043,807

on a rubber mill with 4 parts mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazole and 2 parts sulfur. Shoots of the compounded rubber were cared for 120 minutes at 300° F. Tests run on the cured rubber showed						
the following properties: Tensile strenth	5500 pounds per square					
Blongation at break	inch.					
Modulus at 300% elongation						

Example 7

Shore A durometer hardness.

ìuch.

A polyester was prepared from the condensation reaction of 1 moi of adipic acid, 0.96 mol of ethylens glycol and 0.24 mol of propylens glycol-1,2. This polyester prepared with an approximately 20% excess of glycol had an acid number of 0.5, an hydroxyl number of 59.5 and an average molecular weight of 1870. This polyester (1800 parts) was mixed with 511.3 parts of 4,4'-tolidine dilsocyanate having a purity of 99.5%. The mixture was heated gradually to approximately 100° C. over ture was heated gradually to approximately 100° C, over a period of 85 minutes after which it was permitted to cool. The resulting isocyanate-terminated propolymer (400 parts) was mixed with 78.4 parts of his diviroxy-ethyl n-octenyl succinate and heated for 24 minutes at 100° C. The mixture was then baked in an oven for 11 hours at 120° C. Plasticity tests run on the resulting rubber showed an Olsen flow of 80. The rubber (100 parts) was mixed on a rubber mill with 4 parts mercaptobenzo-thlazyd disulfitie. 1 part mercaptobenzothiazyd disulfitie. 1 part mercaptobenzothiazyd disulfitie. 1 thiazyi cisulfile, 1 part metraprobenzoltiazole, 2 parts sulfur and 15 parts high abrasion furnace black. Shoots of the compounded rubber were cured for 120 minutes at 290° F. Tests run on the cured rubber showed the following properties: Tongila Managh

sensus arcaigro	3800 pounds per.
	square inch.
Elongation at break	700 percent.
Modulus et 300% alongation.	700 pounds per
	square inch.
Shore A durometer hardness	60.
Abrasion	8.5 cubic centimeter

Example 8

A polyester was prepared from the condensation reaction of one mol of adipic acid, 0.96 mol of ethylene glycol and 0.24 mol of propylene glycol-1,2. This polyester, prepared with a 20 mol percent excess of glycol, had an acid number of 0.3, an hydroxyl number of 59.5 and an average molecular weight of 1880. This polyester (1500 parts), was mixed with 401.5 parts of 4,4'-diphenylone methane discovanate and heated gradually to 120° C. for. 114 hours after which it was permitted to cool. The 134 hours after which it was permitted to cool. The resulting knotyanate-terminated prepolymer (527.4 parts) was mixed with 20 parts of crythrol and heated gradually to 100° C, over a 17 minute interval after which it was poured into a pan and baked in an oven for 514 hours at 120° C. The resulting rubber (100 parts) was mixed to with 4 parts mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazyl disulfide, 2 part mercaptobenzothiazyl disulfide, 2 part mercaptobenzothiazyle and 2 parts sulfur. Sheats of the captobenzothiazole and 2 parts sulfur. Sheets of the compounded rubber were cured for 180 minutes at 300° F. Tests showed the cured rubber had the following properties:

Tensile strength	6500 pounds per
Elongation at break	square inch.
Modulus at 300% clongation	375 pounds per square inch.
Shore A durometer hardness	67.

Example 9

70

tion of one mol of adipic acid, 0.96 mol of ethylene glycol, and 0.24 mol of propylens glycol-1,2. This polyester, prepared with an approximately 20 mol percent excess of glycol, had an acid number of 0.5, an hydroxyl traces of given, had an acid number of 0.5, an hydroxyl immber of 58.1 and an average molecular weight of approximately 1920. This polyester (1196.3 parts) was mixed with 332.6 parts of 4.4-td/idine dilsecyanate having a purity of 99.3%. The mixture was heated gradually to approximately 100° C. for one hour after which to was purnified to cool. The resulting isocyanate-terminated prepolymer (1,494.6 parts) was mixed with 62.5 parts of allyl ethylene elvent and heated for 10 minutes. parts of allyl ethylene glycol and heated for 10 minutes at 100° C. after which 3.9 parts of phenyl-beta-naphthylamino were added and heating continued for 5 minutes. The mixture was poured into a pan and baked in an oven for 71/2 hours at 100° C. The resulting rubber was placed on a mill and blended with 3.6 parts of ethyl para-amino benzoate. Plasticity tests run on the rubber showed an Olsen flow of 180. The rubber (100 parts) was mixed on a rubber mill with 4 parts mercaptobenzothiazyl distribution of the rubber mill with 4 parts mercaptobenzothiazyl distributions. on a runper mini with 4 parts intercaptoperizonnezzy of sulfide, one part mercaptoperizothiazote, 2 parts sulfur and 20 parts of high abresion furnace black. Sheets of the compounded rubber were cured for 120 minutes of 300° F. Tests run on the cured rubber showed the fol-25 lowing properties:

.12

	Tenale strength	
30	Elongation at break Modules at 300% elongation	square inch. 620 percent. 1600 pounds per
	Shore A durometer hardness	aquare inch.
	Abrasion	2.5 cubic centimeters per 20 minutes.

. Example 10

A polyestor was prepared from the condensation reaction of one mol of edipic acid, 0.96 mol of ethylene glycol, and 0.24 mol of propylene glycol-1,2. This polycol ester prepared with an approximately 20 mol percent excess of glycol had an acid number of 0.9, an hydroxyl cxccss of grycol had an acid number of 0.9, an hydroxyn number of 56.6 and an average molecular weight of ap-proximately 1950. To the polyester was added 0.01% by weight of magnesium oxide followed by hearing the mixture at 120° C. for 30 minutes. The polyester (800 parts) was mixed with 59.5 parts of bis-(hydroxysthyl) allyl amine. To this mixture was added 214.1 grams of 4.4 tolidine discovanate of 99.2% purity. The completo reaction mixture was heated gradually for 30 minutes to 90° C. after which 2.7 parts of phenyl-beta-naphthylemine were added. Heating was continued for 3 minutes after which the mixture was poured into a part and baked in an oven for 2% hours at 100° C. The resulting rubber (1043 parts) was placed on a rubber mill and blended with 2.6 parts of ethyl para-amino benzoate. Plasticity tests run on the rubber showed an Oisen flow of 267. The rubber (100 parts) was mixed on a rubber mill with 4 parts metcaptobenzothiazyl disulfide, one part of mercaptobenzothiazyle disulfide, one part of high abrasion furnace black. Shoots of the compounded rubber were cured for 20 minutes at 275° F. Tests run on the cured rubbar showed the following properties:

٠.	Tensile strength	
•	•	squaro inch.
	Elongation at break	660 percent.
	Modulus at 300% clongation	1100 pounds per square inch.
	Shore A dirrometer hardness	·63:
١.	Abrasion	4.45 cubic centimeters -
		per 20 minutes

Example 11

A polyestor was prepared from the condensation re-A polyester was prepared from the condensation reac- 7s action of 1 mol of adipic acid, 0.96 mol of chylene gly-

col and 0.24 mol of propylene glycol-1,2. This polyester prepared with an approximately 20 mol percent excess of glycol had an acid number of 0.3, an hydroxyl number of 58.1 and an average molecular weight of approximately 1920. The polyester (364 parts) was mixed with 39 parts of N,N-diallyl melamine and heated gradually for 15 minutes to a temperature of 110° C. after which 100 parts of 4,4'-tolidine disocyanate was added. Heating was continued for 3 minutes after which one part of phenyl-bota-naphthylamine was added. After 2 minutes 10 of additional heating the mixture was poured into a pan and baked in an oven for 3 days at 100° C. Plasticity tests run on the rubber showed an Olsen flow of 121. The rubber (100 parts) was mixed on a rubber mill with 4 parts mercaptobeazothiazyi disulfide, one part mercapto : 16 beazothiazolo, 2 parts sulfur and 20 parts of high-abrasion furnace black. Sheets of the compounded rubber were cured for 60 minutes at 275° F. Tests run on the cured robber showed the following properties:,

__ 1450 pounds per square Tensile strength inch. Hongation at break 540 percent. 1075 pounds per square Modulus at 300% elongation_ inch: Shore A durometer hardness ____. 81.

Example 12

A polyester was prepared from the condensation reaction of one mol of adipic acid, 0.96 mol of cityiene gly-col and 0.24 mol of propylene glycol-1.2. This polyester, prepared with a 20 mol percent excess of glycol, had an acid number of 0.2, an hydroxyl number of 56.5 and an acid number of 0.2, an hydroxyl number of 36.5 and an average molecular weight of spproximately 1985. The polyester (1248 parts) was mixed with 327 parts of 4.4°. 185 tolidine diisocyanate having a purity of 99.5% and heated for 1 hour at 100° C. to 110° C. To the resulting isocyanate-terminated prepolymer (1547 parts) were added 130 parts of pentacrythritol diallyl other. The mixture was heated to 100° C., poured into a pan, placed in an 40.00m and heated for 12 hours at 120° C. Plasticity tests run on the rubber showed an Olsen flow of 91. The rubber (100 parts) was mixed on a rubber mill with 4 carts ber (100 parts) was mixed on a rubber mill with 4 parts mercaptobenzorhiazyl disnifide, 1 part mercaptobenzorhiazyl disnifide, 1 part mercaptobenzorhiazole, 2 parts sulfur, and 20 parts of high abrasion furnace black. Sheets of the compounded rubber were cured for 120 minutes at 290° F. Tests showed the following properties.

Elongation at break Modulus at 300% along the compounded rubber were cured for 120 minutes at 290° F. Tests showed the following properties. lowing properties:

Tensile strength 4200 pounds per square 50 Shore A durometer hardness 70.

Elongation at break 430 percent Example 15

Modulus at 300% clongation. 2700 pounds per square A polyester was prepared from the square of the square o

tion of one mol of adipic acid, 0.96 mol of ethylene gly(col and 0.24 mol of propplene-glycol-1,2. This polyester,
prepared with a 20 mol percent excess of glycol had an
abid number of 0.5, an hydroxyl number of 58.1 and an
average molecular weight of 1920. This polyester (981 56
parts) was mixed with 274 parts of 4.4'-tolidine diisocyanata having a purity of 99.3%. The mixture was gradu(ally heated to a temperature of 100° C, over a period of
(35 minutes and maintained at 100° C, for an additional
(30 minutes and then cooled: To 1236 parts of the resultsing isocyapate-terminated prepolymer were added 71.8
parts of virylcyclohexanediol. The mixture was heated
(pradually to 100° C, over a period of 25 minutes. When
the reaction mixture reached a temperature of 90° C,

mixture was poured into a silicone oil treated aluminum tray and baked for 61/2 hours at 100° C. Plasticity tests run on the rubber showed an Olsen flow of 248. The rubber (100 parts) was inixed on a rubber mill with 4 parts mercaptoberzothiazyl disulfide, 1 part mercaptoparts mercapinoperzonnasyi cusumus, I part interactional parts of high abrasion furnace black. Sheets of the compounded rubber were cured for 180 minutes at 290° F. Tests on the cured rubber showed the following properties:

14

Tensile strength... ---- 4600 pounds per square inch. Elongation at break 580 percent.
Modulus at 300% elongation 1700 pounds per square inch. Shore A durometer hardness... 70. Abrasion 1.5 cubic contineters per 20 minutes.

Example 14

A polyester was prepared from the condensation reaction of a mixture containing 161 pounds of actipic acid, 78.5 pounds of citylene glycol, 29.4 pounds of glycerolalpha-allyl ether, 5.9 grams of magnesium oxide and 122 grams of phenyl-beta naphrlylamine. This polyester prepared with an approximately 35% molar excess of glycol had an acid number of 0.5, an hydroxyl number of 61.8 and an average molecular weight of 1800. The polyester (40,000 parts) was mixed with 5,720 parts 30 of 4,4%-tolidine dissocyanate. The mixture was heated gradually to approximately 172° F. for 7 minutes after which 50 parts of phenyl-beta-naphthylamine was added. The mixture was streed for 3 minutes then proped into taking and baked in an oven for 8 hours at 200° F. Plasaction of a mixture containing 161 pounds of adipic acid, tarray and baked in an oven for 8 hours at 200° F. Piraticity tests run on the resulting elastomer showed a Mooney plasticity (large rotor) of 59. The rubber (100 parts) was mixed on a mill with 2.5 parts of zinc oxide, inpart of stooric acid, 2 parts of mercaptobenzothiazyi disulfide, il part of mercaptohenzothiazole, 1 part of tel-lurium dimethyl dithiocarbamate and 2 parts sulfur. Sheets of the compounded rubber were cared for 20 min-utes at 290° R. Tests run on the cared rubber showed the following properties:

4000 pounds her square inch. Elongation at break 515 percent. Modulus at 300% elongation 2250 pounds per square inch.

Modulus at 300% clongation. 2700 pounds per square inch.

Shore A durometer hardness. 70.

Abrasion. 20 minutes. 70.

Abrasion. 20 minutes. 70.

Example 13

A polyester was prepared from the condensation reaction of not mod of adipic acid, 0.96 mol of ethylene glycular of 0.5, an hydroxyl numbor of 59.0 and an average molecular weight of 1870. The polyester (188.6 parts) was heated to 100° C; Over a period of five minutes the following ingredients were added: 4,4'-toligible discovante (26.4 parts), benzolhiazyl disulfield (6.5) dine discovanate (26.4 parts), benzothiazyl disulfide (6.5 parts), sulfur (2.7 parts) and magneshum oxide (0.05 part). Heating was continued for an additional 30 minutes during which time the temperature rose to 125° C. The mixture was opaque when first formed but ofter a few minutes became almost completely transparent indicating homogeneous bleading of the ingredients. A portion 70 of the mixture was poured onto a metal plate, drawn into a thin film and placed on a hot plate at 160 °C. After one parts of vinyleyclohexanediol. The mixture was heated for the film was cured to a high strength, amber colored, egradually to 100° C. over a period of 25 minutes. When the reaction mixture reached a temperature of 90° C.

3.3 Parts of phenyl-beta-naphthylamine were added. The C. A tightly cured rubbery mass resulted.

8,043,807

col and 0.24 mol of propylene glycol-1,2. This polyester prepared with an approximately 20 mol percent excess of glycol had an acid number of 0.5, an hydroxyl number of 58.1 and an average molecular weight of approximately 1920. The polyester (364 parts) was mixed with 39 parts of N.N-diallyl melamine and heated gradually for 15 minutes to a temperature of 110° C. after which 100 parts of 4,4'-tolldine disocyanate was added. Heating Was continued for 3 minutes after which one part of phenyl-bom-naphthylamine was added. After 2 minutes 10 of additional heating the mixture was poured into a pan and baked in an oven for 3 days at 100° C. Plasticity tests run on the rubber showed an Olsen flow of 121. The rubber (100 parts) was mixed on a rubber mill with 4 parts merceptobenzothiazyl disulfide, one part mercepto- 15 benzothiazole, 2 parts sulfur and 20 parts of high-abrasion furnace black. Sheets of the compounded rubber were cured for 60 minutes at 275° F. Tests run on the cured rubber showed the following properties:

Tensile strength 1450 pounds per square inch. . 540 percent. Elongation at break____ 1075 pounds per square Modulus at 300% elongation_. inch: Shore A durometer hardness 81.

Example 12

A polyester was prepared from the condensation reaction of one mol of adigic acid, 0.96 mol of ethylene glytion of one mot of adipile acid, 0.96 mot of ethylene glycol and 0.24 mot of propylene glycol-1,2. This polyester,
prepared with a 20 mot percent excess of glycol, had an
acid number of 0.2, an hydroxyl number of 56.5 and an
average molecular weight of approximately 1985. The
polyester (1248 parts) was mixed with 327 parts of 4,4'-:38
tolidine dissocyanate having a purity of 99.5% and heated
for 1 hour at 100° C. to 110° C. To the resulting icqcyannte-terminated propolymer (1547 parts) were added
130 parts of pentaerythritol dialtyl ether. The mixture
was heated to 100° C., poured into a pan, placed in an 40
oven and heated for 12 hours at 120° C. Plasticity tests
run on the fubber showed an Olsen flow of 91. The rulber (100 parts) was mixed on a rubber mill with 4 parts
mercaptobenzothiazyl disulfide. I part mercaptobenzothiazole, 2 parts sultur, and 20 parts of high abrasion furance black. Sheets of the compounded rubber were
cured for 120 minutes at 290° F. Tests showed the following properties: lowing properties:

Tensile strength 4200 pounds per square 50 Shore A durometer hardness 70.

Linch 830 percent Rample 15

Modulys at 100% clongation. 2700 pounds per square A polycster was prepared from inch. ٠. Shore A durometer hardness__ 70. 4.7 cubic centimeters per 20 minutes. Abrasion___

Example 13

A polyester was prepared from the condensation reac-tion of one mol of adiple acid, 0.96 mol of ethylene glytion of one mol of adapts acid, 0.96 mol or entylene glycol and 0.24 mol of propylene-glycol-1,2. This polyester,
prepared with a 20 mol percent excess of glycol had an
acid number of 0.5, an hydroxyd number of 58.1 and an
average indiscular weight of 1920. This polyester (981 a6
parts) was mixed with 2.74 parts of 4,4'-tolidine disceysmate having a purity of 99.3%. The mixture was gradually heated to a temperature of 100° C, for an additional
-35 minutes and maintained at 100° C, for an additional
-30 minutes and then populat. To 1236 parts of the results, 70

mixture was poured into a silicone oil treated aluminum tray and baked for 6½ hours at 100° C. Plasticity tests run on the rubber showed an Olsen flow of 248. The rubber (100 parts) was mixed on a rubber mill with 4 parts mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazyl disulfide, 1 part mercaptobenzothiazyle, 2 parts sulfur and 20 parts of high abrasion furnace black. Sheets of the compounded rubber were cured for 180 minutes at 290° F. Tests on the cured rubber showed the following properties:

14

Tensile strength... 4600 pounds, per sqimre inch. . 580 percent. Elongation at break... Modulus at 300% elongation... 1700 pounds per square inch. Shore A durometer hardness... 70. Abrasion..... ... 1.5 cubic centimeters per 20 minutes.

Example 14

A polyester was prepared from the condensation re-action of a mixture containing 161 pounds of adipic acid, 78.5 pounds of ethylene glycol, 29.4 pounds of glycerol-alpha-allyl ether, 5.9 grouns of magnetium oxide and 122 25 grams of phenyl-beta naphthylamine. This polyester prepared with an approximately 35% molar excess of glycol had an acid number of 0.5, an hydroxyl number of 61.8 and an average molecular weight of 1800. The polyester: (40,000 parts) was mixed with 5,720 parts polyester: (40,000 parts) was maken wen 3,720 parts of 4,4'-tolishine discovanate. The mixture was heated gradually to approximately 172. F for 7 minutes after which 50 parts of phenyl-beta-maphhylamine was added. The mixture was stirred for 3 minutes then pound into 12 tray and baked in an oven for 8 hours at 200° F. Plasticity tests run on the resulting clastomer showed a Mooney plasticity (large rotor) of 59. The rubber (100 parts) was mixed on a mill with 2.5 parts of zine exide, lipart of stearic suid, 2 parts of mercaptobenzothinzyl disulfide, 1 part of mercaptobenzothiazole, 1 part of tel-lurium directly dithlocarbemate and 2 parts sulfur. Sheets of the compounded rubber were cured for 20 min-utes at 220° F. Tests run on the cured rubber showed the following properties:

45 Tousile strength Total spirate per square Elongation at break inch. inch. .__. 515 percent. Modulus at 300% elongation... 2250 pounds per square inch.

A polyester was prepared from the condensation reaction of 161 parts of adipic acid, 78.5 parts of ethylene glycol and 29.4 parts of glycerol-sipha-allyl ether in the presence of 0.005 part of magnesium oxide and 0.01 part of phenyl-beta-naphthylamine. This polyester prepared with an approximately 35% excess glycol had an acid number of 0.5, an hydroxyl number of 59.0 and an average molecular weight of 1870. The polyester (188.6 parts) was heated to 100° C. Over a period of five minutes the following ingredients were added: 4.4*tolidine disocvanute (26.4 parts), henopthiavy distribite 66.5 minutes the following ingredients were added: 4.4'stolidine disocyanate (26.4 parts), benzothiazyl disulfide (6.5
parts), salfur (2.7 parts) and magnesium oxide (0.05
no part). Heating was continued for an additional 30
minutes during which time the temperature rose to 125°
C. The mixture was opeque when first formed but after a
few minutes became almost completely transparent indicating homogeneous blending of the ingredients. A portion
of the mixture was poured onto a metal plate, drawn into
a thin film and placed on a hot plate at 160° C. After one
hour the film was rured to a bid strength amber colored and maintest and maintenance at 100° C. for an additional of minutes and then cooled: To 1236 parts of the results of vinyleyclohexanediol. The mixture was leasted a thin film and placed on a hot plate at 160° C. After one parts of vinyleyclohexanediol. The mixture was leasted from the film was cured to a high strength, amber colored, elastomeric sheet. Another portion, powered into an aluminating of phenyl-beta-naphthylamine were added. The 75° C. A tightly cured rubbery mass resulted.

15

In addition to the specific formulations disclosed in the examples above, the clastomeric reaction products of this invention can be compounded in various ways. Cure can be achieved either with stiffur or with peroxides. In general, the sulfur should be present in the formulation to the extent of from 1/2 to 8 parts by weight per 100 parts by weight of the clastomer. Various accelerator parts by weight of the tangent of aid in the cure of these clasioners, it being generally observed that the required level of acceleration is somewhat higher for these clasioners. mers than for natural rubber. It has also been noted that zinc oxide and stearic acid which are almost universally employed as curing sids for natural rubber are not always required to obtain the best physical properties in the clastomers of this invention.

Although the elastomers possess good tensile strength without pigment reinforcement, carbon black has proven to be a particularly effective reinforcing agent for improving the abrasion resistance of the cured polymer. While improvement has been found with as little as 3 parts carbon black by weight, 20 parts based on 100 parts by weight of rubber has proven to be particularly effective in this regard. Other compounding ingredients such as coloring agents, fillers, plasticizers, antioxidents and processing aids may be employed in compounding the 25 elastomer of this invention. In general, it may be said that the compounding of these elastomers presents the same problems faced by the compounding of natural or synthetic rubber. The rubber chemist will vary the came systems and other compounding ingredients in the manner 30 hast maked to being out the absolute proporties desired in best suited to bring out the physical properties desired in the product being made,

If the polymers are to be processed in liquid or malted. form for coatings, films or molded products, the curing agents, accelerators, reinforcing pigments and other compounding ingredients can be added to and mixed with the liquid or melted polymer. In fact, even if a processible clastomer is to be made, it is sometimes desirable to add the compounding ingredients to the liquid reaction product before it forms the solid unvulcanized elatiomer although the curing agents and accelerators should be added on a mix mill after the solid rubber is made if relatively high

temperatures are to be employed during the belging step.
Coring temperatures can be varied from 250° F, to
350° F, but are preferably in the range of from 275° F,
to 310° F, depending upon the level of acceleration employed. The cure times will vary from 10 minutes to 1
hour, it being understood that the higher curing temperatures will permit the development of the desired cored physical properties in the shorter cure times. A cure of 50 and (B) an isocynnato terminated linear polymer pre-30 minutes at 290° F, is generally applicable to most of the elastomers of this invention.

The elastomeric reaction products prepared according to the practices of this invention are useful in manufacturing those products in which natural or synthetic rubber is 56 presently used. In particular they may be used in fabricating tires, belts, hose, sheet packing, gaskets, molded goods, floor mats, dipped goods, sheeting, tank lining, soles, heels; covered rolls, and other mechanical and industrial

While certain representative embodiments and details. have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention. We claim:

1. The reaction product resulting from the reaction of (A) an organic discovanate free of ethylenic unsaturation, (B) the linear polymer prepared from the reaction of at least one dicarboxylic acid free of ethylenic unsaturation containing at least three carbon atoms and at least one bifunctional reactant selected from the group consisting of glycols and dithiols, said linear polymer having an

16 weight of from 900 to 5000; and (C) a third ingredient defined by the formula

in which R is an organic radical inert with respect to the isocyanate groups, X and Y are selected from the group consisting of —OH; —COOH and —SH, and Z is a non-benzanoid sliphatic nonsturated radical selected from the group consisting of $-CH=CH_1$; $-(CH_2)_n-CH=CH_2$ in which n is a whole number from 1 to 10;

CH2-CH=CH2; -CH2-O-CH2--0H;--0--0H;--0=CH; ·

—S—CH₂—CH—CH₃ CH₂—S—CH₂—CH≔CH₃

eaid third ingredient being employed in a sufficient amount to provide at least one pendant non-benzenoid aliphatic unsaturated radical for each 6000 units of molecular weight of said reaction product, the amount of organic disocyanate employed being approximately molecularly equivalent to the sum of the molecular amounts of (B)

and (C).

2. The reaction product as claimed in claim 1 in which C is giveered-alpha-allyl ether.

C is giveron-appn-any; enter.

3. The reaction product as claimed in claim 1 in which
2 is said —(CH₂)_n—CH=CH₂ radical.

4. The clastomeric reaction product resulting from the reaction of approximately equal molecular amounts of (A) an organic compound defined by the formula

in which R is an organic radical inert with respect to the isocyanate groups, X and Y are solected from the group consisting of OH; —COOH and —SH and Z is a nonbanzenoid alignatic unsaturated radical selected from the group consisting of $-CH=CH_2$; $-(CH_2)_n$ $-CH=CH_2$ in which n is a whole number from I to 10;

CH_CH=CH2; --CH2--O--CH₂ -OHI-C-CHI QH.

-CE_-CH=CH; -CH2-S-CH2-CH-CH2,

pared from 2 mols of an organic discovanate free of ethylenic unsaturation, and 1 mol of a linear polymer prepared from the reaction of at least one dicarboxylic acid free of ethylenic unsaturation and containing at least 3 carbon atoms and at least one saturated bifunctional reactant sciented from the group consisting of glycols and dithiols, said livear polymer having an acid number not greater than 5 and an everage molecular weight of from 900 to 5000, the number of pendant unsaturated radicals in said elastomeric reaction product being at least 1 for each 6000 units of molecular weight.

The elastomeric reaction product defined by claim 4 in which (A) is glycerol-alpha-allyl other.

The elastomeric reaction product defined by claim 4 in which Z is — (CH₂)_nCH:—CH₂.

7. A liquid reaction product capable of being vulcanized resulting from the reaction of approximately equal molecular amounts of an organic discovanate free of citylenic unsaturation and at least one linear polymer prepared from the reaction of (A) at least one dicarboxylic acid free of citylenic unsaturation and containing at least 3 carbon atoms and (B) at least one complementary bifunctional reactant selected from the group consisting of glycols and dithiol, said linear polymer having an acid acid number not greater than 5 and an average molecular 75 number not greater than 5 and an average molecular

3,043,807

17

weight of from 900 to 5000, and (C) a third ingredient defined by the formula

in which R is an organic radical inert with respect to the isocyanate groups, X and Y are selected from the group consisting of —OH; —COOH and —SH and Z is a radical selected from the group consisting of

in which n is a whole number from 1 to 10;

said third ingredient being employed in amounts to provide at least one non-benzenoid alighatic unsaturated radical for each 6000 units of molecular weight of said liquid reaction product, the amount of organic discovanate employed being approximately molecularly equivalent to the sums of (B) and (C).

8. The process for preparing clastomeric reaction products which comprises heating to a temperature of approximately 260° F. from 10 to 40 minutes a reaction mixture comprising (A) an organic dilsocyanate free of ethylenic imsaturation, (B) a linear polymer prepared from the reaction of at least one dicarboxylic acid free of linear ethylenic unsaturation and containing at least three carbon atoms and at least one bifunctional reactant selected from the group consisting of glycols and dithiols, said linear polymer having an acid number not greater than 5 and an average molecular weight of from 900 to 5000 and (C) a third ingredient defined by the formula

in which R is an organic radical inert with respect to the isocyanate groups, X and Y are selected from the group consisting of —OH; —COOH and —SH and Z is a nonbenzenoid aliphatic unsaturated radical selected from the group consisting of —CH=CH2; —(CH2)2 —CH=CH2 in which a is a whole number from 1 to 10;

said third ingredient being employed in a sufficient amount to provide at least one pendant non-benzenoid alighatic pusaturated radical for each 6000 units of molecular weight of said reaction product, the amount of organic diisocyanate employed being approximately molecularly equivalent to the sum of the molecular amounts of (B) and (C), heating said reaction mixture at a temperature from 125 to 300° F, while protecting said reaction mixture from contact with the atmosphere to form said electrometric reaction product.

9. The process for preparing elastomeric reaction producis which comprises heating to a temperature of approximately 260° F. from 10 to 40 minutes in the presproximately 200 r. from 10 to 40 minutes it the pres-ence of an ethylene glycol titanate catalyst a reaction mixture comprising (A) an organic discoynante free of ethylenic unsaturation, (B) a linear polymer prepared from the reaction of at least one dicarboxylic acid free of linear ethylenic unsaturation and containing at least 18

three earbon atoms and at least one bifunctional reactant selected from the group consisting of glycols and dithiols, said binear polymer having an acid number not greater than 5 and an average molecular weight of from 900 to 5000 and (C) a third ingredient defined by the formula

in which R is an organic radical inert with respect to the isocyanate groups, X and Y are selected from the group consisting of —OH; —COOH and —SH and Z is a non-benzenoid alignatic unsaturated radical selected from the group consisting of —CH—CH₂; —(CH₂)_m—CH—CH₂ in which n is a whole number from 1 to 10:

said third ingredient being employed in a sufficient amount to provide at least one pendant non-benzenoid alighatic unsaturated radical for each 6000 units of molecular weight of said reaction product, the amount of organic discovenate employed being approximately molecularly equivalent to the sum of the molecular amounts of (B) and (C), heating said reaction mixture at a temperature from 125 to 300° F, while protecting said reaction mixture from contact with the atmosphere to form said electomeric reaction product,

10. A sulfur-curable polymethano solid reaction produst resulting from the reaction of (A) an organic diisocyanate free of ethylene unsaturation, (B) a linear polymer prepared from the reaction of at least one di-carborylic acid free of ethylenic unsaturation and containing at least 3 carbon atoms and at least one bifunctional reactant selected from the group consisting of glycols and dithiols, said linear polymer having an acid number not greater than 5 and an average molecular weight of from 900 to 5000 and (C) glycerol-alpha-allyl other, said glycerol-alpha-allyl other being employed in an amount to provide at least one non-bonsenoid aliphatic unsuturated group for each 6000 units of molecular weight of said polyurethans reaction product, the amount of organic disocyanate being approximately molecularly equivalent to the sum of the molecular amounts of (B)

11. The elastomeric reaction product of claim 1 wherein the third-ingredient is 3-butene-1,2-diol.

References Cited in the file of this patent UNITED STATES PATENTS

	ONIED SINIES FAIRNIS		•
55	2,424,884	Cook et al July 29, 194	7
	2,806,835		7
	2,808,391	Pattison Oct. 1, 195	7
	2,818,404	Hill Dec. 31, 195	7
	2,836,575	Jones et al May 27, 195	8
0	2,858,296	Stilmar Oct. 28, 195	8
	2,888,437	Fincili et al May 26, 195	9
		FOREIGN PATENTS	
15	776,979	Great Britain June 12, 195	7
	863,403	Germany Jan, 19, 195	3

Phoenix, German application Ser. No. P11082, printed January 19, 1956 (K39b 2204), 4 p. spec., no dwg. Farbenfabriken, German application Ser. No. F9661, printed April 26, 1956 (K39c-b), 4 p. spec., no drwg.

OTHER REFERENCES

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,043,807

July 10, 1962

Carl E. Snyder et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as

Column 1, lines 14 and 15, strike out "which are capable of being cured by means of sulfur and"; column 4, line 3, after "minimum of" insert -- non-benzenoid aliphatic --; column octenyl succinate, "insert -- bis hydroxyethyl n-

Signed and sealed this 6th day of August 1963.

(SEAL) Attest:

ERNEST W. SWIDER Attesting Officer

DAVID L. LADD Commissioner of Patents